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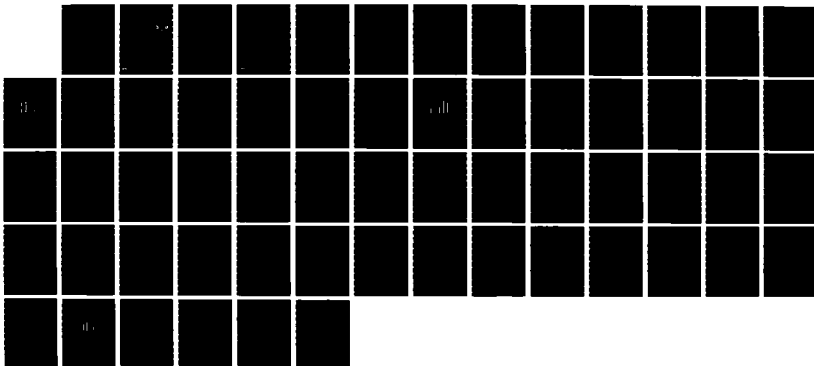
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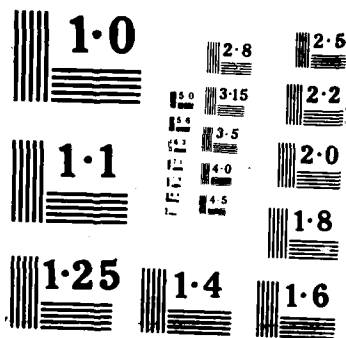
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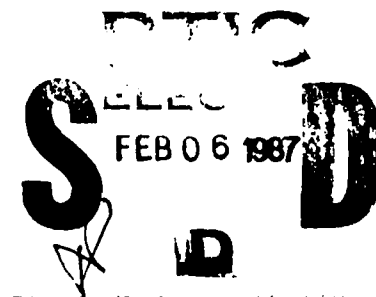
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NITRATION STUDIES IN OXYNITROGEN SYSTEMS

August 1986

Final Report



By: David S. Ross, Georgina P. Hum,
and Chee Liang Gu

Prepared for:

U.S. ARMY RESEARCH OFFICE
P.O. Box 12211
Research Triangle Park, NC 27709

SRI Project DAAG29-83-k-0099

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The research results suggest that new, direct routes to polynitrated materials are available, avoiding the increasing deactivation inherent in successive nitration. The routes could involve the use of 1-electron oxidants, including new photocatalytic semiconductor materials now being developed.					
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August 1986

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and Chee Liang Gu

Prepared for:

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ABSTRACT

SRI has conducted studies in aromatic nitration centered around the direct polynitration of aromatic substrates, avoiding the intermediacy of the lesser nitrated derivatives. The work was prompted by our observation that the lower nitrogen oxide promoted nitration of some aromatic substrates. yielded polynitro derivatives under conditions where the mononitro arene itself did not react.

We have studied the nitration of pyrene in methylene chloride by both N(IV) ($\text{N}_2\text{O}_4, \text{NO}_2$) and N(V) ($\text{HNO}_3, \text{NO}_2^+$), and found, first, that contrary to common belief, N(V) does not nitrate pyrene. The active nitrating agent in the system is N(IV), as the tetroxide. We find the nitration to be first order in pyrene, and first or second order in nitrogen tetroxide with respectively limiting or excess levels of N(IV). We conclude that the mechanism for nitration involves the initial formation of a charge separated pyrene- N_2O_4 complex containing the radical cation of pyrene, followed then by collapse of the complex, or reaction with a second N_2O_4 . In neat, liquid N_2O_4 pyrene is rapidly nitrated to di- and trinitropyrenes, while 1-nitropyrene is nitrated only to dinitropyrenes. The dinitropyrene isomer ratios are different for the two product mixtures, and we conclude that pyrene proceeds directly to the polynitropyrenes without passing through nitropyrene. Indeed it is pyrene rather than nitropyrene that provides trinitropyrene.

Those observations led to a search for such direct di- or polynitration in mixed acid systems. Accordingly we conducted toluene nitrations in 80-90% sulfuric acid media with ^{15}N labeled N(V) and ^{14}N (unlabeled) N(III) under conditions where both mono- and dinitrotoluenes were formed. We first showed that in that acidity region the N(III)-N(V) exchange had a half life of several hours, while the half lives for toluene mono- and dinitration were orders of magnitude faster. In the toluene nitrations we then found that the recovered dinitrotoluenes contained significantly more ^{14}N than did the nitrotoluenes. These results point to a reaction component leading to the

formation of dinitrotoluenes directly, and via N(IV) in line with the pyrene results. In the present case that reaction accounts for 10-20% of the total dinitration.

These findings suggest that new, direct routes to polynitrated materials are available, avoiding the increasing deactivation inherent in successive nitration. The routes could involve the use of 1-electron oxidants, including new photocatalytic semiconductor materials now being developed.



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I INTRODUCTION AND BACKGROUND

The nitro group is a key functionality in energetic compounds, and it has two major virtues. First, the nitro group supplies chemical energy through its significant oxidizing potential. Second, nitro groups are relatively easily introduced into many organic molecules, and in many cases several nitro groups can be put into the same molecule.

Aromatic nitration is one of the oldest and most studied organic reactions. The existence of the nitronium ion was proposed at the beginning of the twentieth century (1), and nitration itself dates back at least 150 years (2a). For decades, the nitration and polynitration of many substrates has been conducted routinely. However, with the increasing sophistication and development of energetic materials science, including the highly broadened structural range of prospective substrates, nitration has become increasingly more difficult.

One significant component of the problem is the introduction of several nitro groups into the same molecule presents. Based on the view of conventional electrophilic nitration, the addition of the first nitro group into an aromatic nucleus severely deactivates the molecule toward the addition of a second. That substitution then results in even greater deactivation, and ultimately an increasingly severe set conditions is required for synthesis of polynitro compounds. This condition applies not only to the nitration of aromatic substrates, but also to amine nitration and the preparation of polynitro-aliphatic compounds.*

SRI's ARO-supported effort in aromatic nitration has focused on the

*Of interest historically, such severe deactivation was the single most important aspect of the reaction in a positive sense. It spurred the growth and industrial development of aromatic nitration because it easily allowed the reaction to be stopped at the desired stages (2b).

nonconventional aspects of aromatic nitration; in particular, we explored the possibility that nitration schemes existed in which polynitration did not take place in a stepwise fashion. Thus we considered a route for nitration proceeding through an intermediate capable of receiving more than one nitro group, and therefore proceeding on the path to a polynitroarene, before the mononitroaromatic itself was formed, and thus before deactivation could become a suppressing factor.

That possibility seemed at least tenable based on our results in the study of "special" or nitrous acid catalyzed nitrations (3a,b). In these cases the nitration of electron-rich aromatic substrates is catalyzed by the lower oxides of nitrogen, and the accelerated nitration proceeds via routes not including prior nitrosation. There has been speculation that these lower nitrogen oxide-catalyzed nitrations involved electron transfer (4a,b), and indeed we showed in gas phase ion molecule studies that the NO_2 /aromatic radical cation pair, rather than the NO_2^+ /aromatic pair, leads to nitroaromatic product (5a,b).

In any case, in our nitration work we observed that under some conditions of lower nitrogen oxide promotion, polynitroarenes were found in the product mixture under condition where the mononitroarene did not nitrate (3b). Our interest in this area culminated in two tasks: (1) pyrene nitration studies, and (2) the direct dinitration of toluene. In the first task, we tried to clarify the role of the various oxides of nitrogen in nitration, including the oxidation states N(III), N(IV), and N(V), by seeking nitration conditions where the various oxides could exist in manageable and kinetically significant quantities.* The conventional mixed acid conditions are inappropriate, since N(IV) readily disproportionates in such media to N(III) and N(V). N(IV), however, is stable in many organic solvents, and accordingly we conducted a study of the kinetics of pyrene nitration in methylene chloride by both N(IV) and N(V). Our efforts followed the considerable

*N(III) = NO^+ , HONO , NO_2^- ; N(IV) = NO_2 , N_2O_4 ; N(V) = NO_2^+ , HNO_3 , NO_3^- .

work of Eberson, Radner and their coworkers in the study of polynuclear aromatic hydrocarbon nitration in methylene chloride with N(IV) (6).

The study included an assessment of the effects of oxygen and NO (N(II)); the results are presented fully in Appendix A as a manuscript, which has been submitted for publication. A summary is presented in Section II. In Appendix B we use our findings for pyrene to explain an anomaly in the levels of mutagenic nitropyrenes in diesel exhaust particulate. This appendix will also be submitted as a manuscript for publication.

These results were next considered in terms of nitration in the more conventional mixed acid medium. In particular, we sought the direct polynitration of toluene in acid media; the results of this study are discussed in detail in Section II.

II RESULTS

Pyrene Nitration Studies.

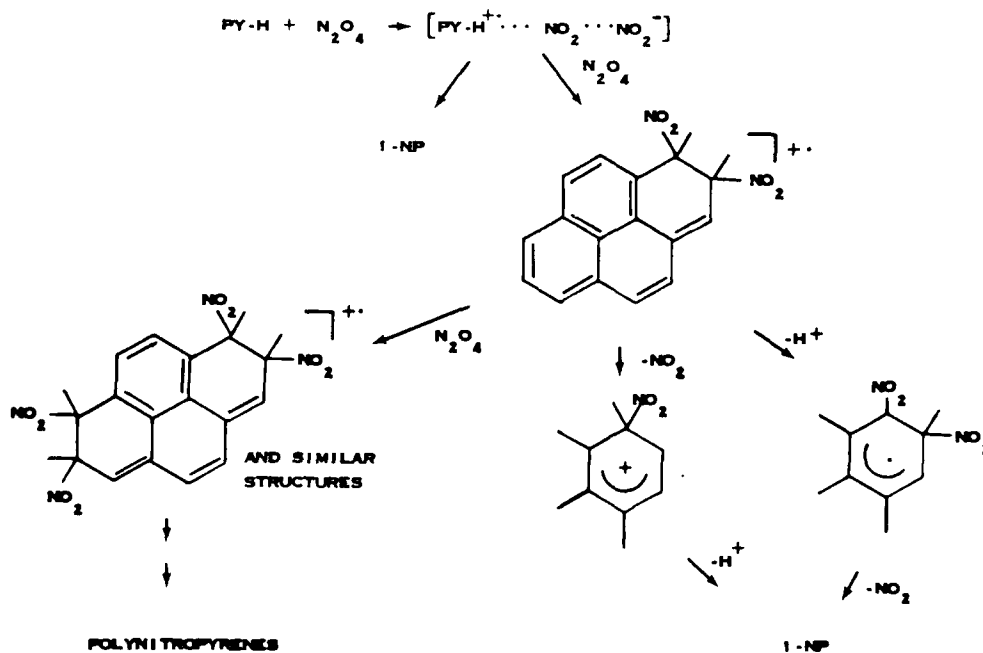
This study, discussed fully in Appendix A, dealt with the kinetics of pyrene nitration, and was conducted primarily in methylene chloride at 25°C. Other media including carbon tetrachloride were also used, and some nitrations were conducted in neat N_2O_4 . In the N(IV) work the concentrations were adjusted so that $N_2O_4 > NO_2$. The kinetics were followed spectrophotometrically in cells designed to allow us to assess the effects of gases such as O_2 and NO .

We began by comparing N(IV) and N(V) nitrations; the results were in contrast to published reports on nitric acid nitration in methylene chloride and similar solvents. It is reported that nitric acid acts as a nitrating agent in these media, performing in a kinetically complex manner with the nitration 5th or 6th order in nitric acid.⁷ The rationale involved nitronium ion as the nitrating species, including kinetically significant nitric acid clusters to support ionization of the acid in the nonpolar medium. The clusters thus explained the high orders in nitric acid.

In contrast, we found that nitric acid did not nitrate pyrene in methylene chloride, at least at rates comparable to the nitration at the same concentration of N(IV). For example, in separate solutions $7-8 \times 10^{-4}$ M in N(IV) and N(V), and 5×10^{-5} M in pyrene, no nitration could be detected in the N(V) case over a period of 1000 sec, whereas in the N(IV) full nitration to 1-nitropyrene (1-NP) was essentially complete in 400-500 sec. In subsequent runs with increased pyrene concentrations, nitric acid began to show some nitration activity, but the action was always considerably slower than for N(IV). In these cases, moreover, the nitric acid nitration came after an induction period, suggesting that pyrene-induced decomposition of N(V) was taking place, producing lower nitrogen oxides including N(IV), which then was responsible for the nitration. (See Figure 1, Appendix A.)

We conclude that the results in the earlier accounts were improperly interpreted. Nitric acid itself is not directly involved in nitration in methylene chloride, and the apparent high orders in N(V) can be explained by a scheme in which nitric acid is partitioned in lower order reactions, only some of which lead ultimately to nitration product.

The N(IV) nitration proceeded handily and was found to be first order in pyrene, and first or second order in N(IV), respectively, when N(IV) was limiting or in excess. The N(IV) species leading to nitration was shown to be specifically N_2O_4 rather than NO_2 in experiments with added NO. A sequence consistent with these results, shown below, is one in which the pyrene undergoes initial 1-electron oxidation by N_2O_4 , with the N_2O_4 dissociating to NO_2 and NO_2^- . There are two competing rate controlling steps: first, collapse of the charge separated complex to product, and second, a parallel step in which a second N_2O_4 reacts with the pyrene radical cation in the complex.

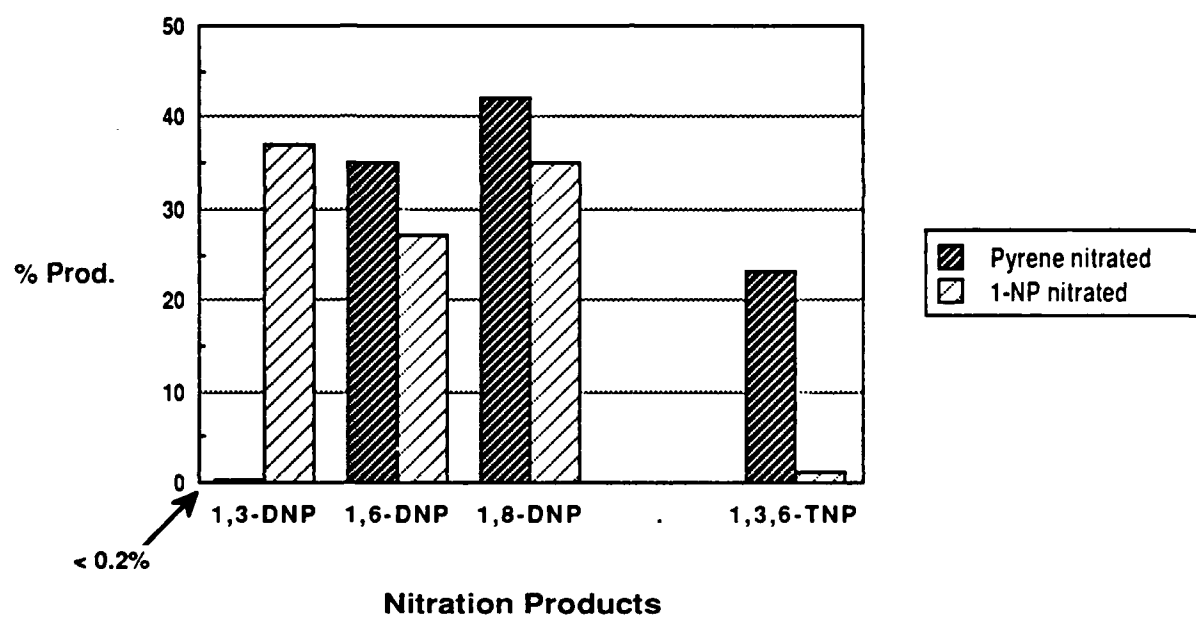


There is precedent for a dissociative 1-electron oxidation like this, including the recent work of Masnovi and Kochi with the tetranitromethane nitration of anthracene,⁸ and the use of I_2 for the generation of radical cations for a wide variety of polynuclear aromatic hydrocarbons.⁹

We tested this scheme by conducting the nitrations in neat N_2O_4 . The key step in the sequence is addition of N_2O_4 to the radical cation. And thus we reasoned therefore that since the product of that addition is still a radical cation, going respectively to a radical or cation only after loss of either H^+ or NO_2 , then with sufficiently high $N(IV)$ concentrations, additional N_2O_4 could add before the H^+ or NO_2 losses occur. Were such a scheme operating, we would then expect to find polynitropyrenes in the product mixture, demonstrating nitration directly to di-, tri- or higher nitrated pyrenes without going through 1-NP. Moreover, the product mixture from pyrene polynitration would probably be different from the nitration of 1-NP itself under the same conditions.

Experiments with pyrene and 1-NP in N_2O_4 fully supported that view, and the results are shown in Figure 1. The reactions were conducted at 25°C, and were complete essentially immediately. No pyrene remained unreacted, and the starting pyrene quantities could be accounted for fully in the products. The pyrene nitration yielded a mixture of 1,6-, 1,8-DNP and 1,3,6-trinitropyrene, with a very small quantity of 1,3-DNP. 1-NP in contrast yielded roughly equal quantities of the 3 dinitropyrene isomers.

This result clearly supports the suggested scheme, demonstrating a route to polynitroarenes that avoids initial nitration. Indeed we see that trinitropyrene is more readily formed from pyrene than from nitropyrene. The 1-NP nitration is itself surprisingly rapid under these conditions, and to the best of our knowledge this result represents the most rapid nitration reported for a nitroaromatic substrate under nonacidic conditions.



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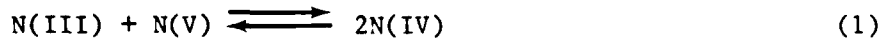
FIGURE 1 PRODUCTS OF NITRATION OF PYRENE
AND 1-NITROPYRENE IN N_2O_4 AT $25^\circ C$

We can make the following conclusions about the nitration of pyrene conducted in nonpolar organic solvents:

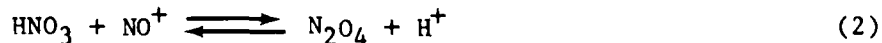
- N(IV) and specifically N_2O_4 , is responsible for the nitration of pyrene and most likely similar aromatic compounds. Nitric acid does not directly nitrate such arenes, at least not at rates comparable to those for N_2O_4 nitration.
- The key to the process is the intermediacy of charge separated species, generated in the present case by the dissociative 1-electron oxidation by N_2O_4 . Presumably other 1-electron oxidants would serve as well.
- One or more N_2O_4 species can add to the initial arene radical cation yielding mono-, di-, and trinitroarenes, and possibly even more highly polynitrated product. The governing factors include the relative rates of the competing N_2O_4 reaction with the radical cation, and loss of either NO_2 or H^+ to the medium.

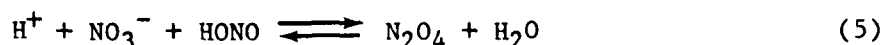
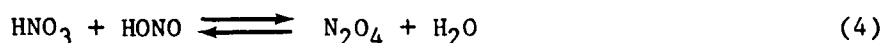
The Direct Dinitration of Toluene

With these results in hand, it was of interest to determine if such chemistry could be operative in mineral acid media, and a study to answer that question was conducted. The steady-state concentration of N_2O_4 in such media is a significant aspect of the question, and the pertinent equilibria can involve several species, depending on the acidity. At sulfuric acid acidities in the range 90%-75% H_2SO_4 , the respective prominent N(III) and N(V) species are NO^+ and HNO_3 . At that point nitric acid begins to be replaced by NO_3^- , and below 60% H_2SO_4 NO^+ is converted to $HONO$. The equilibria leading to N_2O_4 therefore are variations of



and can be one or more of the following



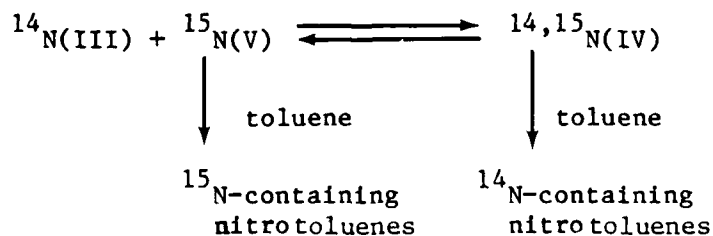


depending on the acidity. The tetroxide of course rapidly dissociates homolytically.



For this study reaction 1 could be a convenient source of N_2O_4 , starting with N(III) and N(V). However, whatever the acidity, it is certain that the steady-state N_2O_4 concentration will be very small, because the ionic and H-bonded oxyacids of nitrogen and their respective conjugate bases will be highly favored in the mineral medium.

Background and Rationale. There are some specific requirements for a study of this sort. Experiments must be designed so that N_2O_4 involvement in nitration can be distinguished from conventional electrophilic nitration by N(V), which of course would be a prominent reaction. Accordingly, we used $\text{Na}^{15}\text{NO}_3$ as the N(V) source, and unlabeled NaNO_2 for the N(III) source. Equal quantities were dissolved in acid media, the salts providing the respective oxyacids. We used toluene as the substrate, and reasoned that the product from conventional sequential electrophilic nitration to dinitrotoluene (DNT) would contain almost solely ^{15}N , with some small quantity of the lighter isotope present because of exchange via reaction (1) before nitration. Any N_2O_4 route to DNT, meanwhile, would yield the product containing significant levels of ^{14}N , the specific ^{14}N quantities being dependent on the relative rates of the two processes.



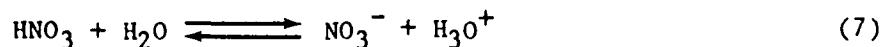
To deal with the exchange problem, we first studied the exchange itself, obtaining rate constants over a range of acidities. The nitration was then studied at acidities and times such that (i) the exchange rate was negligible with respect to di-nitration rate and (ii) both mono- and dinitrotoluenes could be isolated. In that way exchange was not a problem, but at the same time the mononitrotoluene, formed exclusively by N(V), served as a marker displaying the background ^{14}N -content of the N(V).

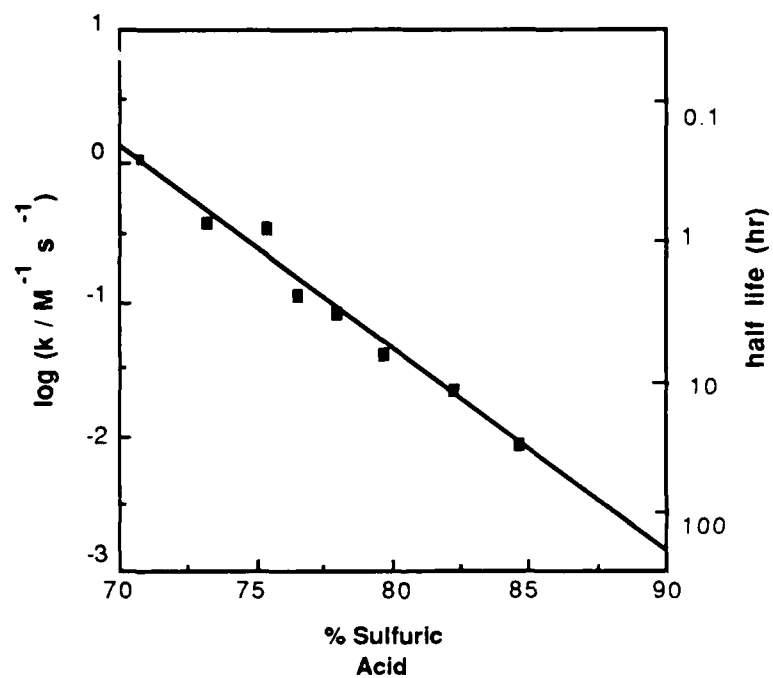
The N(III)-N(V) Exchange. The exchange study was conducted at 25°C over the range 70-85% sulfuric acid, with the N(III) and N(V) solutions both at 1.25×10^{-3} M. The degree of exchange was determined through the N(V) mononitration of toluene, which was essentially instantaneous under these conditions. Aliquots of the acid solution were taken periodically and combined with excess toluene in acetic acid. The nitrotoluenes were recovered and analyzed for ^{14}N and ^{15}N by gas chromatography/mass spectrometry. Excellent second-order data were obtained.

The results are presented in Figure 2, which displays both the values of the second-order rate constants, and the half-lives at the starting concentrations over the range of acidity studied. The exchange at the lower acidities is very rapid, with a half-life of less than a minute at 71% H_2SO_4 . The rate declines with increasing acidity, and at 85% acid the half-life is around 50 hr.

Of the equation series (2)-(5), only eq. (3), with nitrate growing with decreasing acidity, fits this result. The others predict either that the rate would increase with acidity [eq. (5)], or aside from secondary medium effects, be acid-independent [eqs. (2), (4)]. N_2O_4 is thus formed only from the direct reaction of nitrate with nitrosonium ion, most likely initially forming ONO-NO_2 .

In this acidity range, therefore, where N(III) is virtually fully NO^+ , the initial step in the process is

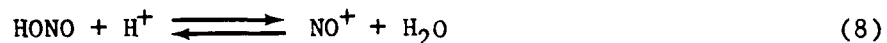




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FIGURE 2 RATE OF $^{14}\text{N}/^{15}\text{N}$ EXCHANGE
AS A FUNCTION OF SULFURIC
ACID ACIDITY

and this step is then followed by (eq. 3), which is rate controlling. We have no data at acidities below 60% sulfuric acid, but we can surmise that the rate of formation of N_2O_4 would reach its peak at around 60% acid; then, at lower acidities where N(III) and N(V), respectively, are essentially fully HONO and NO_3^- , the rate would again decline. In this region, the reaction preceding the NO^+/NO_3^- reaction should be the formation of nitrosonium ion



These results can be used to clarify the mechanism of N_2O_4 hydrolysis, the microscopic reverse of the N(III) + N(V) reaction, which is still not fully understood. Thus despite Carberry's assertion almost 30 years ago that N_2O_4 rather than NO_2 is the reactive species,¹⁰ in a recent review on the kinetics of NO_x dissolution in water, Schwartz and White maintain that at present there are no data available to allow distinction between the two paths (11).

Our data demonstrate that at least in sulfuric acid above 60%, the transition state for hydrolysis contains elements of N_2O_4 and not NO_2 . Acknowledging the absence of data for the lower acidities, it is safe to presume that the NO^+/NO_3^- reaction remains as the significant process in this region, and thus Carberry's view seems correct. However, the lower acid data are needed to confirm this view and unfortunately, the nitration of toluene is not applicable as a diagnostic technique at lower acidities, because the reaction is too slow. We plan to conduct ^{14}N -nmr studies of N(III)/N(V) solutions to provide the necessary data.

Toluene Nitration. After the exchange work, we elected to conduct the DNT study in 82.8% and 87.0% sulfuric acid at 25°C. Solutions of N(III) and N(V), each 6.3×10^{-3} M, were prepared in the two acid media, where the exchange half-lives are on the order of 5 to 50 hr. Then at either 1 min or 10 min after the initial mixing, the solutions quickly received toluene in acetic acid via micropipette, making them 1.25×10^{-2} M in toluene. The half-lives for electrophilic nitration of

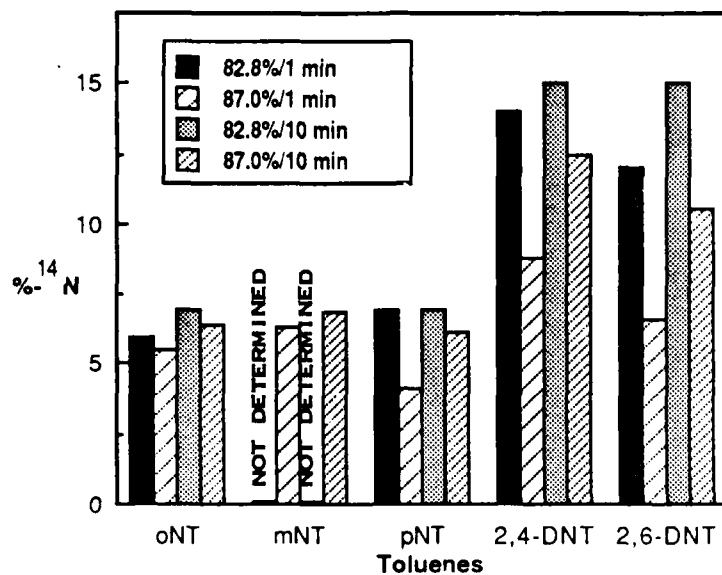
nitrotoluene to DNT can be estimated on the basis of published data to range from 2-3 sec in the weaker acid to around 50 msec sec in the stronger,¹² and clearly under these conditions exchange is of no consequence. The mononitration rates are about six orders of magnitude faster than those for dinitration.

Figure 3 gives the ^{14}N -content of the products for four runs. In each of the four runs, about half of the product mixture was DNT. The ^{14}N -contents of the mononitrotoluenes are 6-7%, and as just discussed that value represents the background quantity of ^{14}N in the N(V) pool. There are no significant differences between the isomers, nor between the 1- and 10-min runs.

The results for the product DNTs, however, demonstrated a direct route to dinitration. The ^{14}N -content is considerably greater in at least three runs, with ^{14}N levels in the 12-15% range. This result shows that N(III) is involved in some way in the dinitration, and can be explained by the direct formation of dinitrotoluene from toluene via chemistry similar to that seen for pyrene, and involving $^{15}\text{NO}_2$ - $^{14}\text{NO}_2$.^{*} The increase in ^{14}N consistent with the direct dinitration supplying 10-20% of the total dinitro product.

The isomer ratios obtained in these runs supported this result. The ratios are summarized in Table 1, and are compared to data from the Radford Army Ammunition Plant for continuous TNT manufacture (13). They are in fair agreement with other published nitration data at lower temperatures (14), and show that temperature has little effect on isomer ratios, at least in these ranges.

* An alternative explanation is that N(III) is in some manner responsible for a portion of the nitration of nitrotoluene. Nitrosation of nitroarenes has not been observed, however, and there is little to support this route.



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FIGURE 3 ^{14}N -CONTENTS OF NITRO- AND DINITROTOLUENES

The mNT's for the 82.8% acid were not determined.

Table 1

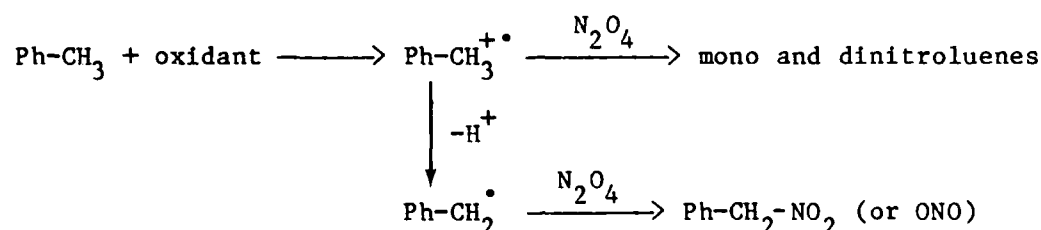
MONO- AND DINITRATIONS OF TOLUENE IN MIXED ACID

<u>Source</u>	<u>Temperature (°C)</u>	<u>Acidity (% H₂SO₄)</u>	<u>Nitrotoluene o/p</u>	<u>Dinitrotoluene 2,6/2,4</u>
This work	25	83-87	0.8-0.9	0.3-0.4
Radford	60-80	70-85	1.7-2.0	0.1-0.2

Both the nitro- and dinitrotoluene isomer ratios are substantially different from the Radford ratios. For the nitrotoluenes, an o/p ratio of around 2 is observed in mixed acid essentially without exception,¹⁴ and our value is around half that. For the DNT, our conditions yield 2-3 times more 2,6- isomer, relative to the 2,4- isomer, than do the Radford conditions.

DISCUSSION

The o/p nitros in Table 1 lead us to reconsider whether the mononitration of toluene is strictly conventional N(V)-driven; in other words, it is possible that both mono- and dinitration have N(IV) components in mineral acid media. In concert with the pyrene case, the direct dinitration of toluene would proceed through the toluene radical cation, in turn generated either by N_2O_4 or N(V), and would then react with N_2O_4 .



There are a number of possible reaction pathways, and in some cases these lead to products we did not find, including α -nitro substitution. More work has to be done to complete the picture; however, our results clearly point to a new mode of nitration operating in both organic and mineral acid media. The reactions are based on the intermediacy of a charge-separated species, which in the organic media may be merely a nonseparated ion pair. In the more polar mineral media, the free radical cation is likely the intermediate.

A radical cation-based, direct polynitration of aromatics opens possibilities for the development of novel nitration procedures. For example, aromatics can be oxidized to radical cations on clays and zeolites. The radical cations of benzene, toluene, and other methylbenzenes, for example, are cleanly formed on the surface of a synthetic mordenite (15). Were this procedure conducted in the presence of N(IV), then the generation of radical cations could lead to the ready formation of polynitroaromatics, including polynitrobenzenes. A variation of that

procedure is the use of photocatalytic semiconductor materials, which can act as 1-electron oxidizers (16). There may be other, more practical surfaces to consider such as soot, which apparently is responsible for the anomalous polynitration of pyrene (Appendix B).

The use of such techniques in nitration, including the substitution of N(IV) for N(V), would have a number of advantages. They include the likely operation of polynitration at ambient temperatures, the absence of the use and reconstitution of strong acids, and most likely a considerable reduction in the quantities of undesirable side products, including oxidized organics and sulfur and nitrogen oxides.

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APPENDIX A

THE NITRATION OF PYRENE BY $\text{NO}_2/\text{N}_2\text{O}_4$

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ABSTRACT

The kinetics of pyrene nitration by N(IV) (NO_2 , N_2O_4) in methylene chloride and under argon have been studied at 25°C, under conditions where the N(IV) was primarily the tetroxide. N(IV) nitrates pyrene directly. The findings demonstrate a process first order in both pyrene and N(IV), with the N(IV) order shifting to 2 with simultaneous increase in starting N(IV) and decrease in starting pyrene concentrations. The nitration is accelerated by the presence of oxygen when $\text{N(IV)} \gg \text{pyrene}$, and retarded when the opposite condition prevailed. At present we have no explanation for that finding. Under conditions where the reaction otherwise produced product in a first order manner, the addition of NO ($\text{NO} \gg \text{N(IV)}$) both shifts the product production to second order, and substantially accelerates the reaction. A scheme consistent with these observations includes the initial formation of a donor acceptor complex between pyrene and N_2O_4 , followed by i) the unimolecular collapse of the complex to product, and ii) addition of a second N_2O_4 to the pyrene in the complex. This second path was shown to lead to polynitropyrenes when the concentration of N(IV) was sufficiently high. The acceleration by NO demonstrates that the radical cation character of the pyrene in the complex is key to the chemistry. Under the same conditions anhydrous nitric acid does not nitrate pyrene. Nitration begins, rather, after a lengthy induction period which appeared to be proportional to the quantity of starting pyrene. Thus PAH-initiated decomposition of the acid to lower oxides including N(IV) brings about nitration.

INTRODUCTION

The nitration of aromatic compounds has been studied for decades, with benzene and its derivatives used almost exclusively as the substrate (1a,b). Nitric acid, usually in sulfuric acid, has generally been the nitrating reagent, with nitronium ion, NO_2^+ , presumed to be the specific nitrating agent. Both are N(V) species.

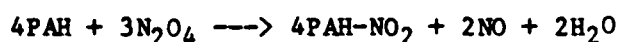
Interest in the study of the nitration of polynuclear aromatic hydrocarbons (PAH) has developed recently, due in part to the significance of combustion-derived nitro-PAH's in the environment (2a-d). The nitration of PAH's in innocuous media such as methylene chloride by N(IV) (NO_2 and N_2O_4) has been of particular interest, since the "textbook" view of aromatic nitration has been via the acid catalyzed route. PAH nitration in N(IV) is surprisingly rapid at ambient temperatures, and both Eberson and Radner (3a,b), and Pryor, et al (4) have focused on electron transfer as key to the reaction.



The study reported on here was prompted by the still unsettled question of just how the reaction takes place. The work includes studies of the reaction kinetics and stoichiometry, and covers the effects of oxygen and NO.

BACKGROUND

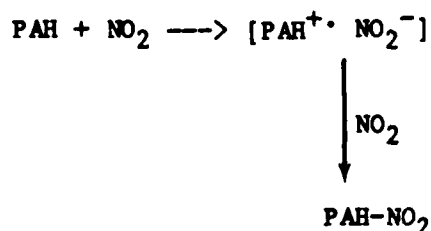
Eberson and Radner have presented a series of papers describing the nitration of PAH's with N(IV). The work dealt with the synthetic and mechanistic aspects (3a), and included study of the reaction of electrochemically generated PAH radical cations with N(IV) (3b, and citations therein). Also covered were the effects of acidic and basic additives, and overall stoichiometry of the reaction was considered to be



The electron transfer aspect of the reaction was looked at using Marcus theory and various thermodynamic cycles. Thus the thermochemistries of a number of electron transfer schemes were considered, and through a series of logical arguments the scheme settled upon was not electron transfer per se, but rather electrophilic attack of PAH by nitrosated nitrogen tetroxide.



A somewhat different picture has been presented by Pryor, et al, who concluded that electron transfer to charge-separated species did occur for some PAH's, with NO₂ as the electron acceptor (4)



The scheme was supported by a correlation found between rate data and results from molecular orbital calculations.

EXPERIMENTAL

Materials: Dichloromethane, (Mallinkrodt) was distilled from calcium hydride before use. Pyrene (Aldrich) was used without further purification. Nitrogen tetroxide (Matheson) was purified with oxygen before use. 100% Nitric acid was prepared by distilling fuming nitric acid from oleum.

Kinetic Measurements: Kinetic runs were conducted under pseudo first-order conditions. The limiting reagent was at a concentration of $\sim 10^{-5}$ M and the excess reagent at 10^{-4} to 10^{-1} M. Fresh stock solutions of the reagents were used. An aliquot of solvent was added to the reaction cell, and aliquots of the pyrene and N_2O_4 stock solutions were added at the desired concentrations. The formation of 1-nitropyrene was monitored at 430 nm on a Hewlett Packard 8450A uv-vis spectrophotometer with a thermostatted cell holder at 25°C. Reactions performed under an atmosphere of argon or oxygen were conducted in a special vacuum cell, designed to allow for degassing of the reactants by freeze-thaw cycles with liquid nitrogen.

Product Analyses: The reaction was scaled up to 10^{-3} M to allow for product analyses. The reaction mixtures were analyzed on a SE-54 capillary column on a Varian 3700 gas chromatograph at 250°C. GC/MS data was obtained on a Hewlett Packard 5890 gas chromatograph with a model 5970 mass selective detector. A DP-1701 capillary column was used at 250°C.

RESULTS

There are a number of aspects of the reaction that require clarification, including the roles of nitric acid, oxygen and NO. Also, while it has been presumed that the reaction is first order each in PAH and N(IV) (3a), there is preliminary evidence that the process may be far more complicated (4). This factor includes consideration of the position of the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium under reaction conditions, and the question of whether NO_2 or N_2O_4 is the primary species.

Included in the work reported below are kinetic studies of the nitration of pyrene by N(IV) in methylene chloride where first the PAH and then the N(IV) were limiting reagents. The study was conducted spectrophotometrically, and in all cases 1-nitropyrene was the sole product, identified by both uv spectrometry and analysis of the product mixture by gas chromatography. The effects of oxygen and NO were determined using a cell designed so that the reaction could be run under argon, with known quantities of these gases added at will.

The degrees of N(IV) dissociation are important to the interpretation of the observed order of the reaction in N(IV). For example, for the sequence



the observation of a reaction, say, first order in N(IV) can be interpreted differently, depending on the major N(IV) species. If the equilibrium step is far to the left, then the N(IV) species in the rate controlling step must be NO_2 . Alternatively if the equilibrium is far to the right, then the N(IV) in the slow step must be N_2O_4 (or two NO_2 's). The problem can become more complicated with observations of reaction orders other than 1.0. Accordingly, using the value of Redmond and Wayland for the equilibrium constant for N(IV) dissociation in CCl_4 of $1.8 \times 10^{-4} \text{ M}$ (5), and the observation that the more polar methylene chloride would support even less dissociation, we can estimate that the N(IV) is far to the side of N_2O_4 at the N(IV) concentrations used here ($5 \times 10^{-5} - 1 \times 10^{-3} \text{ M}$).

Initial Work--Nitric Acid as Nitrating Agent

Due to the large role of nitric acid generally in nitration, it was important initially to establish what its specific place is in nitration in media such as methylene chloride. The acid exists virtually entirely in its molecular form in such solvents, and past accounts of nitrations in such media included complicated kinetics with orders in N(V) up to values of 5-6 (6).

We conducted several nitrations of pyrene in methylene chloride, comparing N(IV) and N(V), and the resulting product/time profiles are shown in Figure 1. In Figure 1a with pyrene as the limiting reactant and the two N-species at the same concentration, it is apparent that on the time scale for N(IV) nitration, nitric acid is unreactive with pyrene. The situation does not change very much when the conditions are

reversed and the N-species are limiting, as shown in 1b. In this case it appears that there is an induction period, during which the nitric acid presumably decomposes to N(IV), which is then responsible for the nitration in some manner. In Figure 1c where the pyrene levels have been increase by a factor of around 20 over those for 1b, the induction period appears to have been overcome, although the reaction in the N(V) case is still considerably slower than the N(IV) reaction. Seemingly the PAH triggers the N(V) decomposition in the initial stages.

No further work was done with N(V) nitration; however we can assert on the basis of these observations that nitric acid itself does not nitrate pyrene in methylene chloride. This finding can be contrasted to the results of Grosjean, et al., who concluded in atmospheric pollutant studies that the opposite view prevailed (2a). Specifically, their results from vapor phase experiments suggested that NO_2 was not active in nitration of filter-deposited PAH, whereas nitric acid was necessary for nitration. The differences in conditions must of course be considered when comparing these data with those from this work. Nonetheless it is difficult to refute the absence of nitration activity by N(V) under our conditions, and the important question of nitrating species in the environmental work remains.

The N(IV) Nitration of Pyrene

Kinetic runs were conducted with both N(IV) and pyrene as limiting reactants, and in each case conducted in both a standard 10 mm uv cell with a smallhead space (~ 3.2 mL liquid volume, ~ 0.5 mL head space), and in our vacuum uv cell with a headspace of around 50 mL. In the

latter case the head gas was 1 atm of argon. As discussed below, the order of addition was important, and in the work described here aliquotes of pyrene stock solutions were added to prepared N(IV) solutions. The results from the two different sets of limiting conditions were surprising, with the orders changing as shown in Figure 2, and summarized in Table 1.

Table 1

Nitration of Pyrene in Methylene Chloride at 25°C

Conditions ^a	Orders
Excess Pyrene P-- 7×10^{-3} - 2×10^{-1} M N-- 7×10^{-5} M	First order in both pyrene and N(IV)
Excess N(IV) P-- 4×10^{-5} M N-- 3×10^{-4} - 2×10^{-3} M	First order in pyrene Second order in N(IV)

a. Ranges of concentration levels at the conditions.
P = pyrene; N = total N(IV) as N₂O₄.

With excess pyrene the production of 1-nitropyrene is first order in both reactants. Thus one set of points in Figure 2 leads to a line with a least squares-derived slope of 1.08 ($r^2 = 0.990$), demonstrating a first order dependence on pyrene concentration. The plot, of course, is the result of points from individual runs yielding profiles clearly first order in product production, demonstrating a first order dependence also on N(IV) concentration. The figure also shows that the choice of cell made little difference.

When the excess reactant is switched to N(IV), the order in N(IV) changes, shown in the figure. The points for the standard cell provide a line with a slope of 1.82 ($r^2 = 0.992$), and under these conditions, therefore, the reaction has changed to a process leaning toward second order in N(IV). The first order product profiles showed that the dependence in pyrene concentration was not changed. Pryor, et al have also noted second order dependence on N(IV) in an account of their preliminary results (4), and this change in order with change in N(IV) concentration demonstrates aspects of the reaction central to the details of the reaction mechanism. One feature of the high order in N(IV) is the need to conduct the kinetic experiments adding the N(IV) to the pyrene, rather than the other way around. We found invariably that the opposite order of addition brought about unpredictable and decidedly unreproducible results.

A cell effect is clearly evident for the N(IV) \gg pyrene case. The rate constants for runs in the cell with the significant headspace are below the linear extrapolation of the line in the plot. Additionally, the ultimate yields of 1-nitropyrene in the gas cell as estimated by the final absorbances were considerably lower than those in the conventional cell. It is evident that the rate of loss of N(IV) out of the medium and into the vapor phase is rapid relative to the nitration rate.

Effects of Oxygen and NO

The potential importance of this chemistry to environmental issues suggested that the effects of O₂ and NO be investigated. The results are summarized in Table 2.

Table 2

Effects of Oxygen and NO on the Nitration of Pyrene in
Methylene Chloride at 25°C

Starting Concn. (M x 10 ⁴)		Head Gas	Observed Order ^a	<u>(s⁻¹ ^{k_{obs} 10⁴)}</u>
<u>N(IV)</u>	<u>pyr.</u>			
<u>Added Oxygen (1 atm)</u>				
<u>Limiting Pyrene</u>				
5.0	0.34	Ar	first	9.1
	0.34	O ₂	"	23.2
6.3	0.34	Ar	"	8.5
	0.34	O ₂	"	52.9
7.5	0.34	Ar	"	11.0
	0.34	O ₂	"	45.1
<u>Limiting N(IV)</u>				
0.68	141	O ₂	no easily defined rate law	
<u>Added NO (22 torr)</u>				
0.67	280	Ar	second	2.2 ^b

a) Order observed in the product-production profile.

b) Observed second order rate constant, $10^4 \times M^{-1} s^{-1}$.

The results of runs with added O₂ under conditions of limiting pyrene show clearly that O₂ increases the rate of nitration under these conditions. In these cases the product production was first order. However when the condition is switched to limiting N(IV), the effect of added oxygen also switches, as is shown in Figure 3. Here, the O₂ severely slows the nitration, and the product profile reflects no simple

rate law. The profile can be reasonably well matched with a process 6th-order in N(IV), a result reminiscent of the high order in nitric acid mentioned earlier (6). However a more likely explanation is a reaction or reactions operating parallel to, and competitive with nitration, and in which the pyrene or the N(IV) is consumed in a process not yielding nitropyrene. (It can be shown that product profiles from parallel first order reactions can mimic higher order reactions.) Consistent with this surmise is the observation that yields of 1-nitropyrene from the O₂-runs, as demonstrated by the product profiles like that in Figure 3, were found to be considerably below quantitative.

The effect of added NO is more straightforward. In a single run under argon, 22 torr of NO were added to the gas cell. The cell contained 5 mL of a methylene chloride solution 2.8×10^{-2} M in pyrene and 6.7×10^{-5} M in N(IV), and on a molar basis NO \gg N(IV). In this case the development of product smoothly followed second order behavior, in contrast to the first order production of 1-nitropyrene under the same conditions, but in the absence of NO.

This result is in line with the simple scheme depicted in reactions 1-2, with N(IV) virtually fully nitrogen tetroxide, and with the tetroxide as the specific species reacting with pyrene. The addition of NO drives the N(IV) almost fully to N₂O₃, and thus the N₂O₄/NO₂ balance is shifted to favor the dioxide. As expected from the scheme, when NO₂ becomes the major form of N(IV) present in the system and with N₂O₄ the reacting species, the production of product shifts from first to second order.

However the reaction rate must be accounted for. If the equilibrium levels of the tetroxide are responsible for the nitration, then what must be a very small value when NO is present dictates that product formation be accordantly very slow. The fact that the product production rate is similar to that with no added NO demonstrates that NO itself must take part in the reaction. It has been shown that NO readily forms stable pi-complexes with aromatic radical cations (7), and we can surmise, therefore, that such species are part of PAH nitration, yielding with NO the NO-pyrene⁺ complex, which is then readily converted to nitropyrene.

Headspace Effects and Stoichiometry

In the earlier accounts of pyrene nitration by N(IV) it was shown that NO was a prominent reaction product, and that each N₂O₄ ultimately yielded 1-1/3 nitropyrenes (3a,4). Our experience included the substantial effects of NO on reaction rate, as just discussed, and also effects of head space on nitropyrene yields, as estimated spectrophotometrically. Specifically we found in the runs with pyrene >> N(IV) that with a large headspace the nitropyrene/N₂O₄ ratio ranged from 0.9 to 1.3, while with little head space ratio approached and in some cases exceeded 2.0.

Accordingly, a study of the reaction stoichiometry was conducted using gas chromatography for analysis, and the results are summarized in Table 3.

Table 3

STUDIES ON THE STOICHIOMETRY OF PYRENE NITRATION
BY N(IV) IN METHYLENE CHLORIDE

Starting Quantities (umoles)		Mass Balance (%)	1-Nitropyrene/ N ₂ O ₄
Pyrene	N(IV)		
79.1	7.6	97.5	2.4
109.8	15.1	94.3	1.8

The two factors to consider are the mass balances and the yield ratios. The former are satisfactory, and the latter are less so. In other words we can account for the carbon-containing components of the mixture, but the range in the ratios reflects some difficulty in introducing N(IV) to the system with adequate precision. It is evident from these results, however, that in our hands the pyrene/N₂O₄ ratio must be closer to 2.0 than it is to 1.3.

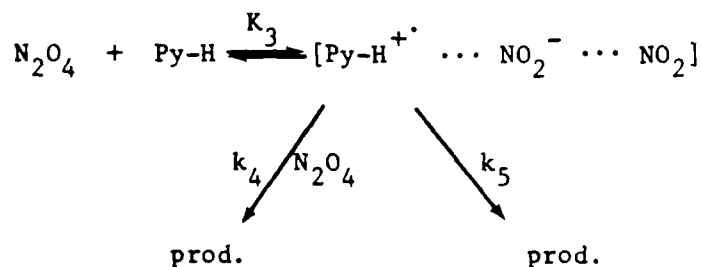
Thus with limiting N₂O₄, both NO₂'s are accounted for in the nitropyrene product. This result dictates that there be some component in the ² system which can act as a sink for hydrogen. We have considered that pyrene itself might act as an oxidant, but while our starting pyrene contains some quantities of dihydropyrene (DHP), we find that there is no significant increase in DHP after a run. We also considered that the methylene chloride medium might be the ultimate H-sink, but a careful search for HCl after nitration was negative. At present we suspect small quantities of oxygen to be responsible, even though we made every effort to eliminate O₂ from the system, and this aspect of the work remains to be clarified.

DISCUSSION

The accumulated evidence for the nitration of pyrene includes the facts that in methylene chloride, nitric acid does not directly nitrate pyrene, while N(IV) readily does. With limited pyrene and under the condition $N_2O_4 > NO_2$, the reaction is second order in the tetroxide. The order shifts to first order with declining N(IV) concentration and/or increasing pyrene concentration, at levels where the tetroxide is still maintained as the major N(IV) species. The view that the tetroxide rather than the dioxide is the specific reactant is supported by the observation that with added NO, which shifts the condition to $NO_2 > N_2O_4$, the production of product shifts from a first order to a second order process. Less directly explainable are the effects of the purposeful addition of oxygen, which either accelerates or slows the nitration, respectively, with limiting pyrene or N(IV).

Reaction Scheme and Rate Algebra

A scheme which can account for these observations is presented below. It includes the initial, rapid and reversible formation of a pyrene- N_2O_4 donor-acceptor complex; such complexes have been well documented (8,9).



The pyrene in the complex then reacts with a second N_2O_4 to yield product in step 4. In a parallel step, the complex in step 5 breaks down yielding the same product.

There are two variations of this scheme, both of which explain the reaction order behavior. In the first, the large span in pyrene concentrations used here of about 4 orders of magnitude is considered to shift the initial equilibrium from one favoring the starting materials to one favoring the complex. In this case from a kinetics point of view step 5 is not necessary, and the starting material effectively is the complex itself. The second possibility is one where equilibrium 3 is always virutally fully to the left, and the complex is partitioned between steps 4 and 5. In both cases we would expect the order in $N(IV)$ to shift from 1 to 2 with simultaneous increase in starting $N(IV)$ and decrease in starting pyrene levels.

An expression for the observed rate constant, k_{obs} , can be derived for the scheme for the case of limiting pyrene ($c_{N_2O_4}$ = concentration of nitrogen tetroxide),

$$k_{obs}/c_{N_2O_4} = K_3k_4c_{N_2O_4} + K_3k_5$$

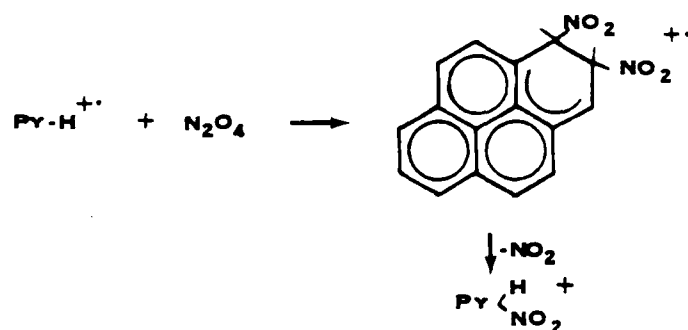
and a plot of $k_{obs}/c_{N_2O_4}$ vs $c_{N_2O_4}$ provides a test of the proposed mechanism. The plot should yield a line passing through the origin if step 5 is unimportant, and with a non-zero intercept if step 5 is significant. As shown in Figure 4, such a plot does provide a reasonably sound line ($r^2 = 0.96$), and the non-zero intercept shows that the second route is operative. The slope and intercept respectively give the values: $K_3k_4 = 5585 \text{ M}^{-2} \text{ s}^{-1}$; $K_3k_5 = 3.2 \text{ M}^{-1} \text{ s}^{-1}$.

Reaction Mechanism

The pyrene in the charge-separated complex has radical cation character, while the N_2O_4 can dissociate to accommodate its radical anion character. Direct electron transfer from PAH to both NO_2 and N_2O_4 was considered by Eberson and Radner, but was rejected on the basis of their Marcus theory calculation (3a). However the dissociative detachment-like process suggested here, i.e., $N_2O_4 + e^- \rightarrow NO_2 + NO_2^-$, should overcome the objections posed by the calculations. This approach is the condensed phase, nonphotochemical analog to that proposed by Masnovi and Kochi for the reaction between anthracene and tetranitromethane, in which electron acceptance by the latter was accompanied by the formation of NO_2 and trinitromethide anion (10).

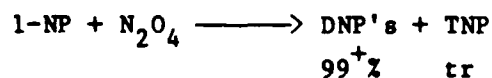
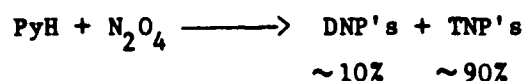
The radical cation character of the complexed PAH leads to its reaction with NO_2 , provided either within the complex or externally, and leading to a classical Wheland (sigma) intermediate. This cationic species must lose a proton to some base present in the system in a step following the rate controlling one (11). The fact that an external source of N(IV) can compete with that available in the complex suggests that radical character to the NO_2 in the complex is compromised somewhat by the partial negative charge shared by both halves of the nitrogen oxide.

Alternatively, the second N_2O_4 in step 4 could add to the system, leading to intermediates which could then lose NO_2 to yield the Wheland intermediate



To test this possibility, in a small scale experiment we allowed small quantities of solid pyrene to react with liquid N_2O_4 at ambient temperatures. Were the addition of the tetroxide to the radical cation an important reaction route, it was reasoned that in neat N_2O_4 perhaps more than one would add, and polynitropyrenes would be formed.

That view was readily confirmed. The reaction was virtually instantaneous, and essentially quantitative. A mixture of trinitropyrenes was isolated, containing small quantities of dinitropyrenes. (WARNING: These compounds are highly mutagenic.) Next, 1-nitropyrene itself was treated in the same way, and in this case virtually quantitative yield of a mixture of 1,3- 1,6- and 1,8-dinitropyrenes was identified, with small quantities of trinitropyrenes present.



This observation adds further support to the radical cation- N_2O_4 addition route, since from these results it is clear that the trinitropyrenes from pyrene could not have been formed via nitropyrene.

To our knowledge this procedure is the most simple route to these materials, the reported methods involving high temperature and concentrated nitric acid, and sometimes providing only modest yields (dinitropyrenes, 12a; trinitropyrene, 12b). Further we are aware of no more mild nitration of an aromatic compound already containing a nitro group, and the reaction of 1-nitropyrene here most likely also proceeds through a donor-acceptor complex with N_2O_4 .

The conventional acid-promoted nitration of pyrene to the dinitro-aromatic yields the 1,6- and 1,8- isomers (13). However on the basis of the rules of electrophilic nitration, these isomers should be formed in the minority, if at all, since they would result from sigma-cationic intermediates with contributing structures containing positive charges adjacent to a nitro group (11). Thus the chemistry discussed here must be operative in acid nitration media as well. This point raises an interesting contrast to the position taken by Eberson and Radner (3a). Their thesis is that the nitrous acid catalyzed (NAC) nitration observed for electron rich substrates in acid media is that operative with N(IV) in methylene chloride. We agree that the two processes are the same, but view what is termed NAC in acid media as being, rather, the N(IV) nitration described here.

The effects of oxygen we observed cannot be fully explained. However it is not unreasonable to expect the chemistry related to the

charge separation be affected by oxygen, since donor-acceptor complexes between aromatic hydrocarbons and O_2 itself are known (14). The formation of HONO in the nitration ultimately leads to the 1-1/3 stoichiometry reported by other workers. As described by Eberson and Radner, the HONO decomposes to water, NO and NO_2 . However in our case, the NO must be oxidized by oxygen or other oxidants present in the system back to NO_2 . Alternatively the HONO itself could be oxidized; its reaction with oxygen in solution is reported to be very rapid (15).

Acknowledgement

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FIGURE CAPTION

Figure 1. COMPARISON OF N_2O_4 AND HNO_3 .

a) HNO_3 /pyrene = $7.5 \times 10^{-4} M / 4.9 \times 10^{-5} M$; N_2O_4 /pyrene = $8.4 \times 10^{-5} M / 5.7 \times 10^{-5} M$.

b) HNO_3 /pyrene = $2.9 \times 10^{-5} M / 1.5 \times 10^{-2} M$; N_2O_4 /pyrene = $5.1 \times 10^{-5} M / 1.5 \times 10^{-2} M$.

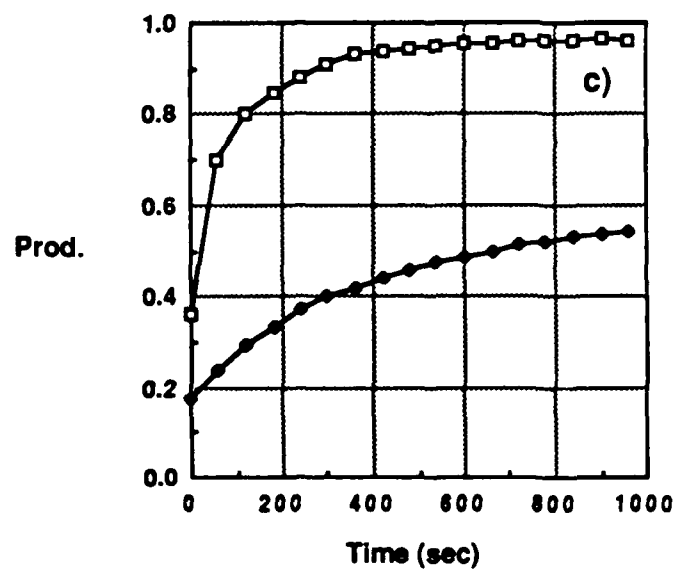
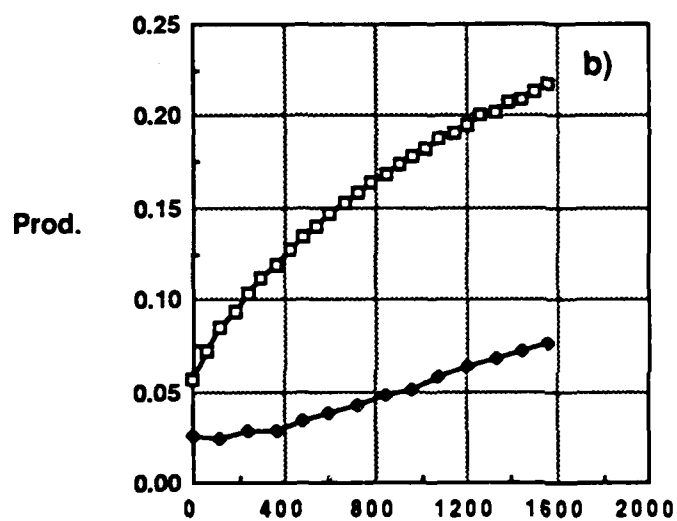
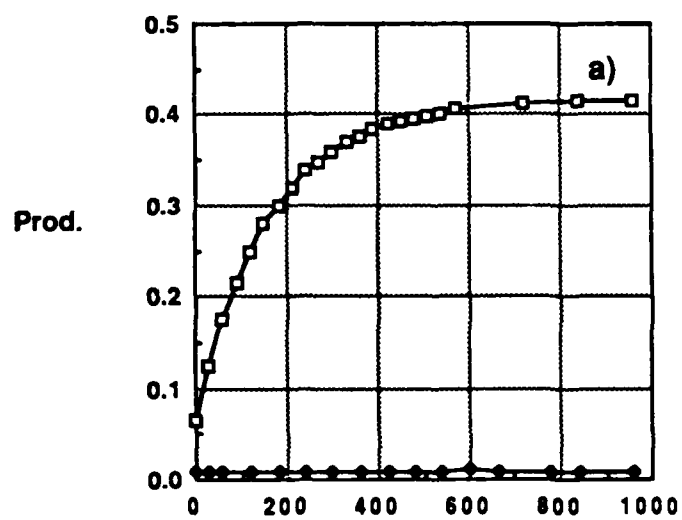
c) HNO_3 /pyrene = $5.3 \times 10^{-5} M / 2.8 \times 10^{-1} M$; N_2O_4 /pyrene = $7.3 \times 10^{-5} M / 2.6 \times 10^{-1} M$.

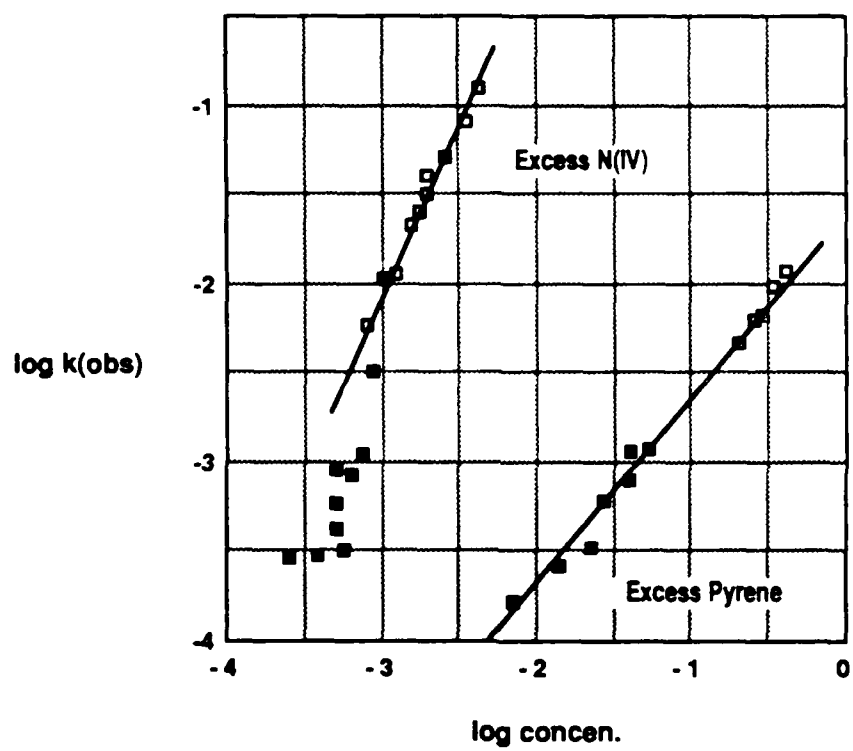
Figure 2 DETERMINATION OF REACTION ORDER. Abscissa values correspond in each case to the concentration of the reactant in excess.

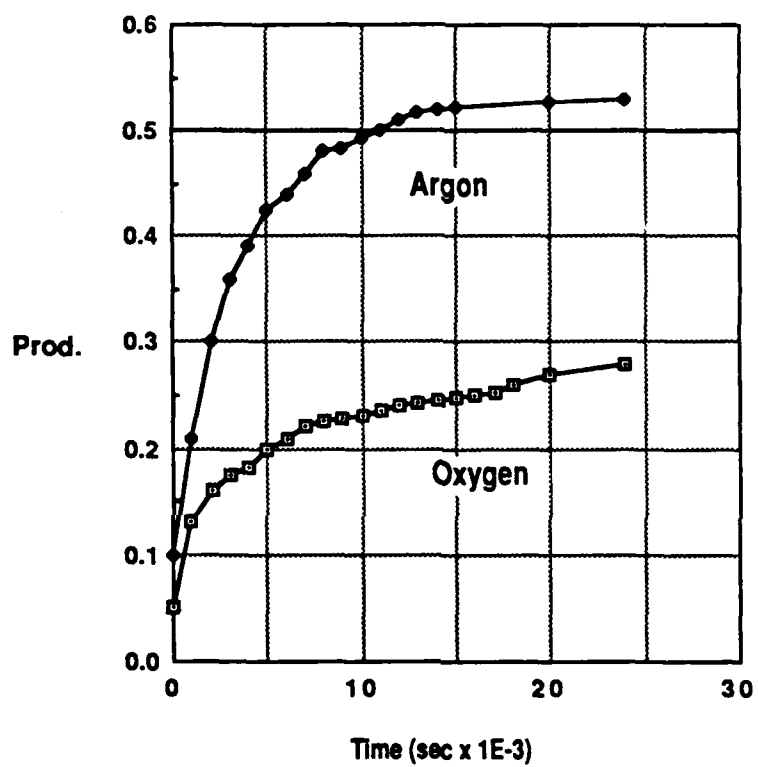
□ - conventional cell; ■ - vacuum cell

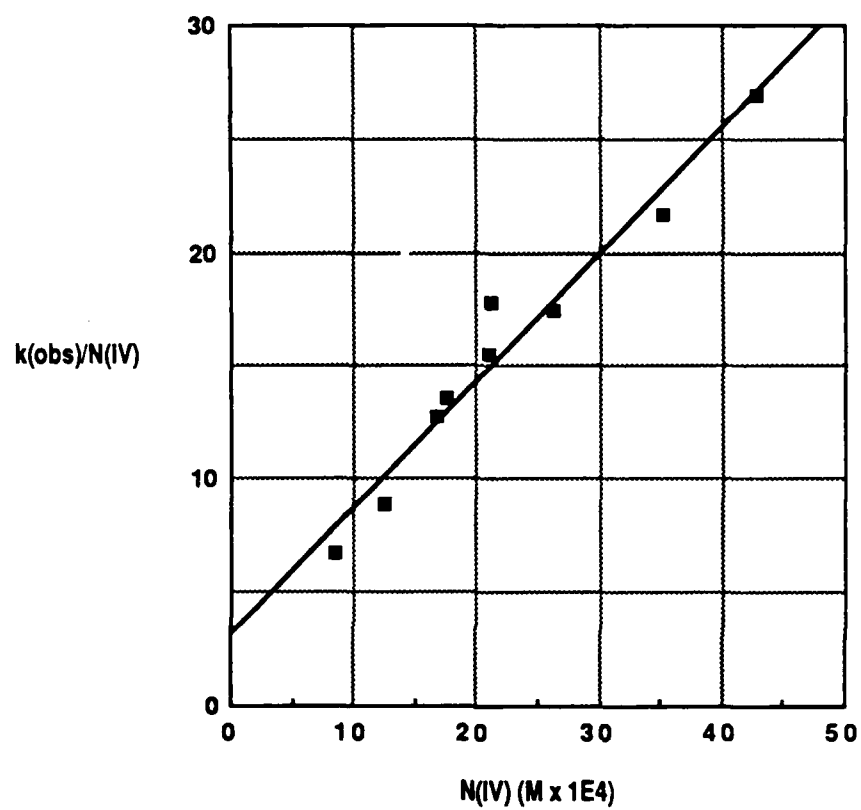
Figure 3. EFFECTS OF OXYGEN IN PYRENE NITRATION. Pyrene = $1.4 \times 10^{-2} M$; N_2O_4 = $6.8 \times 10^{-5} M$. Argon and oxygen both at 1 atm.

Figure 4. PLOT OF $k_{obs}/N(IV)$ vs $N(IV)$.









Appendix B

THE NITRATION OF PYRENE

The mutagenic activity of diesel exhaust particulates is an area of present concern and study. Nitroarenes are detected in exhaust extracts, and 1-nitropyrene (1-NP) and the 1,6- and 1,8-dinitropyrenes (1,6-; 1,8-DNP) are three of the several candidates considered as the significant mutagens (Jensen et al., 1985). In fact, 1,8-DNP is the most mutagenic compound known, with the 1,6-isomer only slightly less active (Rosenkranz and Mermelstein, 1985).

Pyrene (P) itself is a major extractible component of diesel exhaust particulate, and is found typically in quantities two to three orders of magnitude greater than 1-NP (Henderson et al., 1984). In turn the DNP levels are usually two orders of magnitude below 1-NP (Jensen et al., 1985). Thus in round numbers $\text{DNP:NP:P} = 10^{-5}:10^{-3}:1$.

The fact that $\text{P} \gg \text{NP}$ demonstrates that the nitrating agent is present in limiting quantities ($\text{P} \gg \text{NO}_x$) (Henderson T. R. et al., 1984; Williams P. T. et al., 1986). Under such conditions however, the anticipated conventional sequence $\text{P} \rightarrow \text{NP} \rightarrow \text{DNP}$ cannot be responsible for the dinitroarenes, as discussed below. We conclude that there must be another source for the polynitroaromatic products.

The inconsistency is demonstrated from the kinetics aspects of conventional electrophilic nitration and the action of nitric acid (Schofield, 1980). Thus the addition of a first nitro group to an aromatic system brings about a six-order-of-magnitude decrease in the rate of substitution of a second.* Using this value in calculations based on consecutive second-order reactions (Frost A. and Pearson R. G.,

*This value can be estimated from the data at 25°C for the nitric acid nitrations of toluene (Coombes et al, 1968) and p-nitrotoluene (Vinnik et al, 1967) in 80% sulfuric acid.

1965), it can be estimated that at conditions where both the nitrating agent is limiting and unnitrated arene remains in the product mixture, the ratio dinitroarene:mononitroarene should be in the range of 10^{-10} - 10^{-13} , or far below what is observed. Even lowering that estimate somewhat to account for the use of toluenes rather than PAH for the rate differences, it is clear that the levels of dinitropyrenes in diesel exhaust are far too high for DNP to be formed in conventional electrophilic nitration.

Some insight into how the polynitroarenes are formed may lie in results from our recent study of the nitration of pyrene. We studied the actions of HNO_3 and of N(IV) [$\text{NO}_2/\text{N}_2\text{O}_4$] under conditions where $\text{N}_2\text{O}_4 > \text{NO}_2$. The work was conducted in both methylene chloride and in condensed, neat N(IV) . The substrates were pyrene and 1-nitropyrene, and the reactions were studied both in the presence and absence of oxygen. The study included the kinetics of nitration and the distribution of products formed under various conditions (Ross D. S., Hum G. P., and Schmitt R. J., 1986).

This work gave two results important to the present question: (i) under our conditions, N(IV) and not nitric acid nitrates pyrene, and (ii) nitropyrene is not an intermediate in the formation of polynitropyrenes from the pyrene/ N(IV) reaction. The former finding runs contrary to several recent reports (summarized by Chan and Gibson, 1985). However, our findings, the results of competitive runs with comparable concentrations of N(IV) and anhydrous HNO_3 , are unequivocal. Some data are presented in Figure 1; in Figure 1(a) it is seen that with nitric acid no nitration takes place at periods where full nitration occurs at comparable $\text{NO}_2/\text{N}_2\text{O}_4$ levels. Only after a considerable excess of arene is present does nitration take place, as shown in 1(b) and 1(c), demonstrating that the arene-promoted decomposition of nitric acid leads to $\text{NO}_2/\text{N}_2\text{O}_4$, which then nitrates the arene.

As regards the intermediacy of nitropyrene, we found that in neat N(IV) pyrene rapidly forms di- and trinitropyrenes, whereas under the same conditions 1-nitropyrene equally rapidly forms primarily dinitropyrenes, with only a trace of the trinitro derivative (Figure 2).

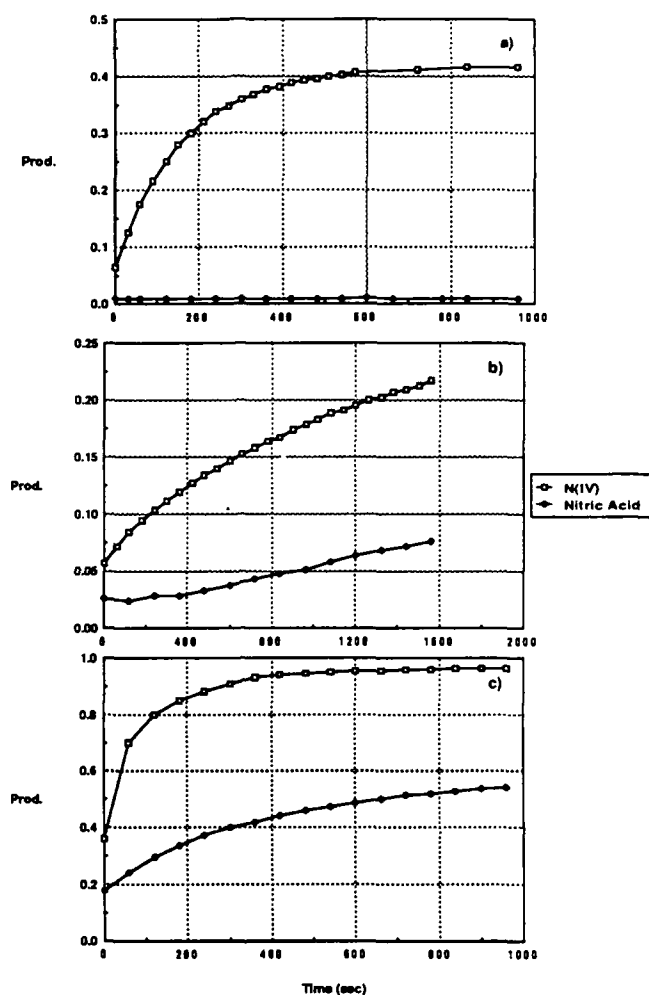


FIGURE 1 COMPARISON OF N_2O_4 AND HNO_3 NITRATIONS.

a) HNO_3 /pyrene = $7.5 \times 10^{-4} M / 4.9 \times 10^{-5} M$; N_2O_4 /pyrene = $8.4 \times 10^{-5} M / 5.7 \times 10^{-5} M$.

b) HNO_3 /pyrene = $2.9 \times 10^{-5} M / 1.5 \times 10^{-2} M$; N_2O_4 /pyrene = $5.1 \times 10^{-5} M / 1.5 \times 10^{-2} M$.

c) HNO_3 /pyrene = $5.3 \times 10^{-5} M / 2.8 \times 10^{-1} M$; N_2O_4 /pyrene = $7.3 \times 10^{-5} M / 2.6 \times 10^{-1} M$.

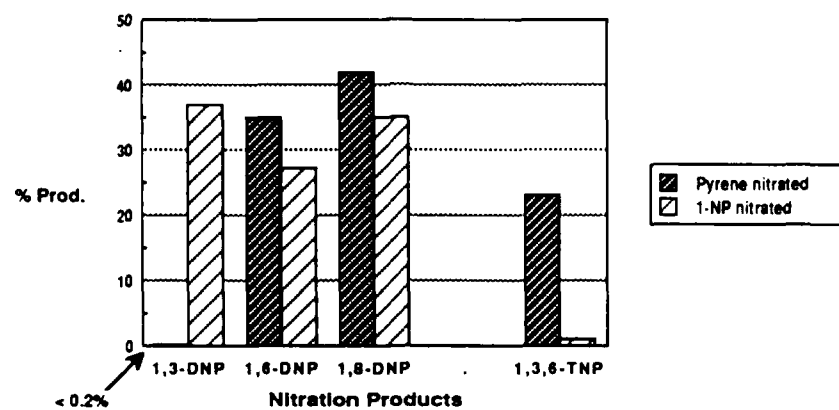
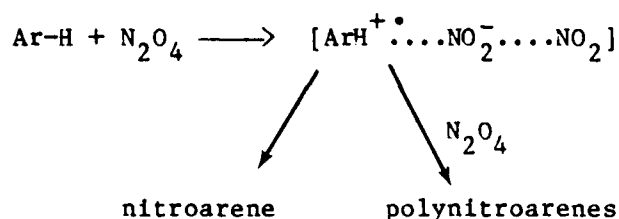


Figure 2. PRODUCTS OF NITRATION OF PYRENE AND
1-NITROPYRENE IN N_2O_4 AT $25^{\circ}C$.

Moreover, the dinitropyrene distributions from the two nitrations are very different. Thus nitropyrene is not an intermediate in the production of the more highly nitrated pyrenes from pyrene. Accordingly, we conclude that pyrene, and presumably other PAH substrates, can proceed directly and rapidly to polynitrated arenes, skipping over lower nitrated species.

We have explained these findings with a reaction scheme involving initial 1-electron oxidation of the arene by molecular N_2O_4 , followed by reaction of the radical cation-like arene intermediate with one or more additional tetroxides



(Ross, et al., 1986). Because the N_2O_4 nitration is so rapid, we presume that 1-nitropyrene goes through a similar sequence; however, as shown in Figure 2, it yields different product mixtures.

We can conclude therefore that the DNPs in diesel exhaust arise from this kind of chemistry. In a diesel engine exhaust train, however, the N(IV) must be virtually fully dissociated ($\text{NO}_2 \gg \text{N}_2\text{O}_4$), and accordingly there must be other source of the arene radical ion. We can surmise that the surfaces of the exhaust soot particles or perhaps other surfaces in the system could generate such species; it is known, for example, that some clay or zeolite surfaces can generate arene radical cations (Kurita Y., Sonoda T., and Sato M., 1970). However the issue at present remains unresolved.

Finally, it is of interest to consider the recent results of Grosjean and coworkers (Grosjean D., Fung K., and Harrison J., 1983). They found under conditions of limited nitrating agent that the nitration of PAHs by $\text{NO}_2/\text{N}_2\text{O}_4$ was suppressed when the arenes were deposited on diesel soot, and that nitric acid was necessary for the nitration.

Because our studies show that nitric acid does not directly nitrate PAH, the observations of Grosjean et al. require another explanation. We assert that the observed suppression was rather the result of the consumption of the limited $\text{NO}_2/\text{N}_2\text{O}_4$ by rapid reaction with the soot support. In other words, the soot is more reactive toward nitration than is the PAH, a result consistent with the observations of Smith et al. (1984); moreover, because the nitrating agent was limiting, the support rather than the substrate reacted. The apparent enhancement of nitration by the addition of nitric acid is thus due to its decomposition on the soot surface, both deactivating the surface toward nitration, and yielding N(IV) , which then brings about the arene nitration.

In their work on the reactions of soot with $\text{NO}_2/\text{N}_2\text{O}_4$, Smith and coworkers showed that C-NO_2 , C-O-NO_2 , and C-N-NO_2 groups were readily introduced onto the surface (Smith D. M., Akhter M. S., and Chughtai A. R., 1984). These results suggest that the particulate surface itself in diesel exhaust could be mutagenic, and could be one component in the unaccounted-for toxicity of diesel exhaust.

NOTE

This appendix is a preliminary version of a note to be submitted to Environmental Science and Technology.

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